

# The ground state of the $\text{H}_3^+$ molecular ion: a physics behind

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## Abstract

Five physics mechanisms of interaction leading to binding of the  $\text{H}_3^+$  molecular ion are identified, realized in a form of variational trial functions and their respective total energies are calculated. Each of them provides subsequently the most accurate approximation for the Born-Oppenheimer (BO) ground state energy among (two-three-seven)-parametric trial functions being correspondingly,  $\text{H}_2$ -molecule plus proton (two variational parameters),  $\text{H}_2^+$ -ion plus H-atom (three variational parameters) and generalized Guillemin-Zener (seven variational parameters). These trial functions are chosen following a criterion of physical adequacy, they include the electronic correlation in the exponential form  $\sim \exp(\gamma r_{12})$ , where  $\gamma$  is a variational parameter. Superpositions of two different mechanisms of binding are investigated and a particular one, which is a generalized Guillemin-Zener plus  $\text{H}_2$ -molecule plus proton (ten variational parameters), provides the total energy at the equilibrium  $E = -1.3432$  a.u. Superposition of three mechanisms: generalized Guillemin-Zener plus ( $\text{H}_2$  -molecule plus proton) plus ( $\text{H}_2^+$  -ion plus H) (fourteen parameters) leads to the total energy which deviates from the best known BO energy to  $\sim 0.0004$  a.u. In general, our variational energy agrees in two-three-four significant digits with the most accurate results available at present as well as major expectation values.

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## I. INTRODUCTION

We had learned recently from Takeshi Oka about a fundamental importance of the two-electron hydrogenic molecular ion  $\text{H}_3^+$  in Physics, Chemistry and Astronomy [1], in particular, that is a system of the lowest total energy among ones made from protons and electrons. The ion  $\text{H}_3^+$  is one of the most abundant chemical compounds in the Universe being a major proton donor in chemical reactions in interstellar space. Experimentally, the  $\text{H}_3^+$  was discovered by J.J. Thomson in 1912 [2]. From another side, being theoretical physicists we are not aware about any popular quantum-mechanical textbook as well as a book on spectral theory where the  $\text{H}_3^+$  molecular ion is even mentioned. Even though the  $\text{H}_3^+$  as the simplest three-center problem plays the same role of a fundamental object as the hydrogen and helium atom being the simplest one-center problems, and  $\text{H}_2^+$  and  $\text{H}_2$  being the simplest two-center problems. Needless to say that such a role implies to use  $\text{H}_3^+$  as a test ground for different theoretical approaches.

In general, the Coulomb system  $(3p, 2e)$  is very difficult for theoretical studies. Many theoretical methods were developed to study low-lying quantum states of this system. In particular, it became clear very quickly that interelectron correlation is of great importance and it has to be included into the variational trial function explicitly to assure a faster convergence. This conclusion is similar to one drawn by Hylleraas [3] for the He atom, and by James and Coolidge [4] for the  $\text{H}_2$  molecule. Usually, the interelectron correlation was written in a form of monomial  $r_{12}^n$  (Hylleraas [3] - James-Coolidge [4] form) or  $\exp(-\alpha r_{12}^2)$  (Gaussian form, see e.g. Ref. [5]). Recently, Korobov [6] showed in an explicit way that for the case of the Helium atom the use of the exponential form  $\exp(-\gamma r_{12})$  dramatically improves convergence and leads, in fact, to the most accurate results for the ground state energy for the Helium atom at present. Later on, it was shown that the similar use of the exponential correlation  $\exp(-\gamma r_{12})$  for the  $\text{H}_2$  molecule allows us to construct the most accurate trial function among the few-parametric trial functions [7]. A hint of why this  $r_{12}$ -dependence leads to the fast convergent results was given in [7].

In 2006, the Royal Society discussion meeting on  $\text{H}_3^+$  took place in London, UK (see [1]) and at 2012 the Royal Society Theo Murphy Meeting on  $\text{H}_3^+$  held where different properties of the  $\text{H}_3^+$  ion and, in particular, various theoretical approaches to a study of the  $\text{H}_3^+$  ion were presented (see [8]). It is worth mentioning that the benchmark results for the potential

energy surface of  $\text{H}_3^+$  were reported by Adamowicz - Pavanello [9].

The goal of this contribution is twofold: (i) to study a physics of binding, and based on that (ii) to propose a maximally simple, compact and easy-to-handle trial function with few (non)linear parameters which would lead to a highly accurate Born-Oppenheimer ground state energy and major expectation values. We always assume that two-Coulomb charge effective interaction in a presence of other Coulomb charges is modeled by  $e^{-\alpha r}$ , where  $\alpha$  is a parameter (which is a lowest Coulomb orbital for the case of opposite charges), since a corresponding potential reproduces a Coulomb singularity at small distances and vanishes at large distances. Perhaps, it is worth noting that we are not aware of previous studies of the  $\text{H}_3^+$  ion with trial functions involving  $r_{12}$  in an exponential form with a single exception [10] where the  $\text{H}_3^+$  in a linear configuration in a magnetic field was explored. This paper can be considered as a continuation of a study of different physics mechanisms of binding started at [11], where two possible mechanisms of binding and their superposition were explored (not dominant ones).

In this paper atomic units ( $\hbar = e = m_e = 1$ ) are used throughout.

## II. THE $\text{H}_3^+$ ION IN THE BORN-OPPENHEIMER APPROXIMATION

The Hamiltonian which describes the ion  $\text{H}_3^+$  under the assumption that the protons are infinitely massive (the Born-Oppenheimer approximation of zero order) and located at the vertices of an equilateral triangle of side  $R$  (see Fig. 1 for the geometrical setting and notations), is written as follows:

$$\mathcal{H} = \sum_{j=1}^2 \frac{\hat{\mathbf{p}}_j^2}{2} - \sum_{\substack{j=1,2 \\ \kappa=A,B,C}} \frac{1}{r_{j,\kappa}} + \frac{1}{r_{12}} + \frac{3}{R}, \quad (1)$$

where  $\hat{\mathbf{p}}_j = -i\nabla_j$  is the 3-vector of the momentum of the  $j$ th electron, the index  $\kappa$  runs over protons  $A$ ,  $B$  and  $C$ ,  $r_{j,\kappa}$  is the distance between the  $j$ th electron and the  $\kappa$ th proton,  $r_{12}$  is the interelectron distance, and  $R$  is the interproton distance.

It is a well established fact that the ground state of the  $\text{H}_3^+$  molecular ion is  $1^1A'_1$ , an electronic spin-singlet state, with the three protons forming an equilateral triangle in the totally symmetric representation  $A'_1$  of a  $D_{3h}$  point symmetry [12]. Thus, the ground state electronic wavefunction should be symmetric under permutations of the three indistinguishable protons. This ground state is the major focus of the present study.

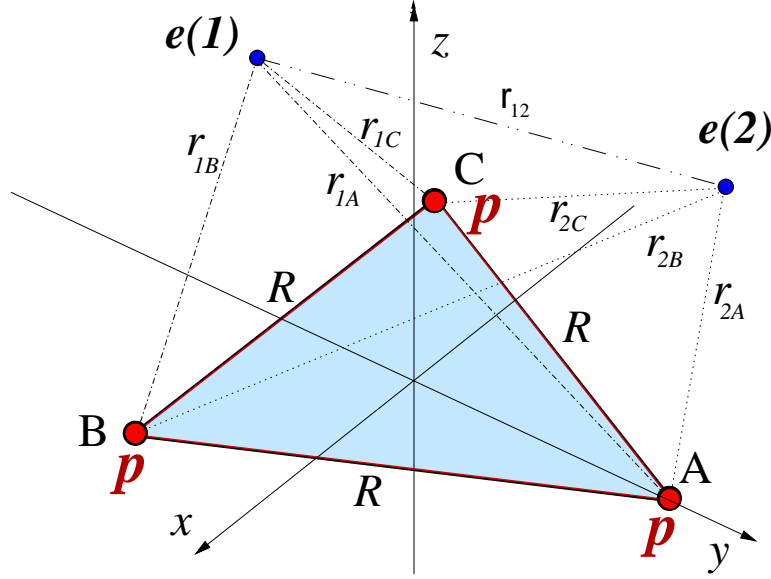


FIG. 1: Geometrical setting for the hydrogen molecular ion  $\text{H}_3^+$  in equilateral triangular configuration. The three protons are located on the  $x$ - $y$  plane forming an equilateral triangle with the origin of coordinates located at the geometrical center (circumcenter) of the triangle.

It is worth mentioning that the best theoretical value at the moment for the Born-Oppenheimer ground state energy is  $E = -1.34383562502$  a.u. [13] obtained with a basis of 1000 explicitly correlated spherical Gaussian functions with shifted centers. This value surpasses the previous record  $E = -1.343835624$  a.u. by Cencek *et al.* which was obtained by using explicitly correlated Gaussian functions [14].

### III. VARIATIONAL METHOD

We use the variational procedure to explore the problem. The recipe for choosing the trial function is based on arguments of physical relevance, e.g. the trial function should support the symmetries of the system, has to reproduce the Coulomb singularities and the asymptotic behavior at large distances adequately (see, e.g. [15–17]). To the problem finding a bound state of  $(3p, 2e)$  giving rise to  $\text{H}_3^+$  molecular ion we follow the description given in [11].

In practice, the use of such trial functions based on physical adequacy implies the convergence of a special form of the perturbation theory where the variational energy is the sum of

the first two terms of the perturbation series. Let us recall the essentials of this perturbation theory (for details, see [15–17]). Let us assume that the original Hamiltonian has a form  $\mathcal{H} = -\Delta + V$ , where  $\Delta$  is the Laplacian. As a first step we choose a trial function  $\psi^{(trial)}$  (normalized to one) and find a potential for which such a trial function  $\psi^{(trial)}$  is an exact eigenfunction, *i.e.*  $V_{trial} = \Delta\psi^{(trial)}/\psi^{(trial)}$ , with energy  $E_{trial} = 0$ . In a pure formal way we can construct a Hamiltonian  $\mathcal{H}_{trial} = -\Delta + V_{trial}$  such that  $\mathcal{H}_{trial}\psi^{(trial)} = 0$ . It can be easily shown that the variational energy

$$E_{var} = \langle \psi^{(trial)} | \mathcal{H} | \psi^{(trial)} \rangle$$

is nothing but the first two terms in the perturbation theory where the unperturbed problem is given by  $\mathcal{H}_{trial}$  and the perturbation is the deviation of the original potential  $V$  from the trial potential  $V_{trial}$ , namely,  $V_{perturbation} = V - V_{trial}$ . Eventually, we arrive at the formula

$$E_{var} = E_{trial} + E_1(V_{perturbation}) , \quad (2)$$

here  $E_1(V_{perturbation}) = \langle \psi^{(trial)} | V_{perturbation} | \psi^{(trial)} \rangle$  is the first energy correction in the perturbation theory, where the unperturbed potential is  $V_{trial}$ . It is worth noting that if the trial function is the Hartree-Fock function, the resulting perturbation theory is nothing but the Moeller-Plesset perturbation theory (see, e.g. [19], Section 15.18)<sup>1</sup>.

One of the criteria of convergence of the perturbation theory in  $V_{perturbation} = V - V_{trial}$  is a requirement that the ratio  $|V_{perturbation}/V|$  should not grow when  $r$  tends to infinity in any direction. If this ratio is bounded by a constant it should be less than one. In fact, it is a condition that the perturbation potential is subordinate with respect to the unperturbed potential. The value of this constant controls the rate of convergence - a smaller value of this constant leads to faster convergence [16]. Hence, the above condition underlines the importance of the large-range behavior of the trial functions. In the physics language the above requirement means that the phenomenon of the Dyson's instability should not occur (for a discussion see [15])<sup>2</sup>.

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<sup>1</sup> It is worth noting that the question about convergence of the Moeller-Plesset perturbation theory is not settled yet [20]

<sup>2</sup> It is worth noting that this procedure for a selection of the trial function was applied successfully to a study of one-two-electron molecular systems in a magnetic field leading to highly accurate results. Many of these results are the most accurate at present (see [17] and [18]).

In order to make the above-mentioned criteria of convergence concrete for the problem of  $\text{H}_3^+$  let us introduce the exponential representation of the spin-singlet ground state function

$$\Psi(x) = (1 + P_{12}) \sum_{\text{perm}\{A,B,C\}} e^{-\varphi(r_{1A}, r_{1B}, r_{1C}, r_{2A}, r_{2B}, r_{2C}, \gamma r_{12})} , \quad (3)$$

where  $\varphi(r_1, r_2) \equiv \varphi(r_{1A}, r_{1B}, r_{1C}, r_{2A}, r_{2B}, r_{2C}, \gamma r_{12})$  is unknown phase. If (3) is substituted to the Schroedinger equation a non-linear equation of a type of the multidimensional Riccati equation will occur. The analysis of the behavior of  $\varphi$  at large distances along any direction in six-dimensional physical space  $\mathbf{R}^6$  leads to the asymptotics of the form

$$\varphi \rightarrow ar + O(\log r) , \quad r \rightarrow \infty , \quad (4)$$

where the constant  $a$  can depend on the chosen direction, while the behavior near a Coulomb singularity  $r_C$  of the potential is

$$\varphi \rightarrow br + O(r^2) , \quad r \rightarrow r_C , \quad (5)$$

where  $b$  makes sense of a cusp parameter (residue at the Coulomb singularity). Hence, a trial function with a phase  $\varphi_{\text{trial}}$  which grows linearly at large distances guarantees a convergence of the perturbation theory where the chosen trial function is considered as zero approximation. Furthermore, for such a choice the ratio  $|\varphi_{\text{trial}}/\varphi_{\text{exact}}|$  is bounded. Actually, this property implies that relative accuracies in energy and in an expectation value may not be very much different.

There are the different ways to include electronic correlation explicitly in the trial wave function for two-electron problems. We mention three major approaches (see e.g. [21]): the linear in  $r_{12}$ , the gaussian  $\exp(-\alpha r_{12}^2)$  and exponential  $\exp(\gamma r_{12})$  terms. Among them, the only factor  $\exp(\gamma r_{12})$  fulfills the physical adequacy requirements for a trial function described above and may lead to a convergent perturbation theory.

#### IV. PHYSICS MECHANISMS OF BINDING

As an illustration to what follows let us describe physics mechanisms of binding of the simplest two-center, one-electron molecular system  $\text{H}_2^+$ . There are three of them: (i) a coherent interaction of electron with two centers, (ii) incoherent interaction of electron with two centers, and (iii) a general, screened interaction of electron with two centers. A simplest

realization of these three mechanisms leads to the celebrated Heitler-London function (the product of two lowest, equally screened Coulomb orbitals, the electron "sees" two centers simultaneously), Hund-Mulliken function (the sum of two lowest, equally screened Coulomb orbitals, the electron "sees" one center only, it corresponds to the interaction H-atom with proton), and Gullieimin-Zener function (the symmetrized product of two lowest, unequally screened Coulomb orbitals, the electron "sees" both centers but differently). A linear superposition of these three functions gives the accuracy of order of  $10^{-5}$  for any separation (see e.g. [17]).

Following the guidelines of Section III and the convergence requirement of the perturbation theory, the most general trial function for the ground state made out of individual exponentials is of the form:

$$\psi_G = (1 + P_{12}) \sum_{\text{perm}\{A,B,C\}} e^{-\alpha_1 r_{1A} - \alpha_2 r_{1B} - \alpha_3 r_{1C} - \alpha_4 r_{2A} - \alpha_5 r_{2B} - \alpha_6 r_{2C} + \gamma r_{12}}, \quad (6)$$

see Fig.1 for notations, where the sum runs over the permutations of the identical protons  $A, B, C$  ( $S_3$  symmetry), and  $P_{12}$  is the operator which interchanges electrons ( $1 \leftrightarrow 2$ ). The variational parameters consist of non-linear parameters  $\alpha_{1-6}$  and  $\gamma$  which characterize the (anti)screening of the Coulomb charges. The interproton distance  $R$ , see Fig.1 is kept fixed and all there distances are chosen to be equal, thus, protons form equilateral triangle,  $R = R_{eq} = 1.65$  a.u. [10-11]<sup>3</sup>. The function (6) is a symmetrized product of  $1s$  Slater type orbitals multiplied by the exponential correlation factor  $e^{\gamma r_{12}}$ .

Calculations of the variational energy were performed using the minimization package MINUIT from CERN-LIB. Six-dimensional integrals which appear in the functional of energy were calculated numerically using a "state-of-the-art" dynamical partitioning procedure. The calculations were made in double-cylindrical coordinate system:  $(x_1, y_1, z_1, x_2, y_2, z_2) \rightarrow (\rho_1, \phi_1, z_1, \rho_2, \phi_2, z_2)$ . As the first step the infinite domain of integration was reduced to a finite, compact domain in a form of two 3D cylinders in such a way that a contribution from the complement should be two orders of magnitude smaller than the requested absolute accuracy of integration. As the second step the domain of integration was subdivided into

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<sup>3</sup> Almost all previous calculations were carried out for the same value of  $R_{eq}$ . It is justified by the fact that the minimum of the potential curve in  $R$  is very flat being characterized by a small curvature. Hence, for a given accuracy in energy the accuracy of localizing the position of the minimum is much lower (see Table I)

972 up to 6534 subdomains following the profile of the integrand, in particular, separating out the domains with sharp changes of the integrand, the domains of the large gradients. Then each subdomain was integrated separately in a parallel manner with controlled absolute/relative accuracy (for details, see e.g. [17]). A realization of the routine required a lot of attention and care. During the minimization process both the domain and partitioning were permanently controlled and adjusted. Numerical integration of every subdomain was done with a relative accuracy of  $\sim 10^{-3} - 10^{-7}$  depending on its complexity and relative contribution using an adaptive routine based on an algorithm by Genz and Malik [22]. This is an adaptive multidimensional integration routine (CUBATURE) of vector-valued integrands over hypercubes written by Steven G. Johnson with a vectorized prototype prepared by Dmitry Turbiner, <http://ab-initio.mit.edu/wiki/index.php/Cubature> . Parallelization was implemented using the MPI library MPICH. Computations were performed on a Linux cluster with 48 Xeon processors at 2.67 GHz each, and 12Gb total RAM plus an extra processor serving as the master node. The complete minimization process for every Ansatz took from 100 (single Ansatz, Eqs. (6-11), see below) up to 2000 (triple mechanism Ansatz, Eq. (16), see below) hours of aggregated wall clock time. A single integration was about from 1 up to 15 minutes. With optimal values of parameters, it took about 60 minutes (wall clock time) to compute a variational energy (calculating two integrals) with relative accuracy  $10^{-7}$ .

### A. Single mechanism

A goal of subsection is to identify some possible single mechanisms of interactions which occur in the system of three static protons and two electrons, ( $3p2e$ ).

#### 1. Coherent interaction

One of the most natural mechanisms of interaction is when each electron "sees" all charged centers simultaneously, coherently interacting with them. Such a mechanism has to be dominant at small internuclear distances in comparison with a characteristic length of the electron-proton interaction which seems to be of the order of 1 a.u. = 1 Bohr radius. A simplest realization of this mechanism in a wavefunction is given by a product of Coulomb



	Trial Function	$E$ (Ry)	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$\alpha_5$	$\alpha_6$	$\gamma$
1.	Coherent	-2.583	0.5711	0.5711	0.5711	0.5711	0.5711	0.5711	0.29783
2.	Incoherent	-2.595	1.3557	0	0	0	1.3557	0	-0.06136
3.	$H^- + 2p$	-2.148	1.3284	0	0	1.3284	0	0	0.25244
4.	$H_2 + p$	-2.634	0.9422	0.9422	0	0.9422	0.9422	0	0.43977
5.	$H_2^+ + H$	-2.650	0.9114	0.9114	0	0	0	1.2499	0.04359
6.	Generic	-2.680 7	-0.00353	0.18548	1.4245	1.0471	0.15082	0.58912	0.21632

TABLE I: The ground state energy of the  $(3p2e)$  system in different mechanisms of binding realized by Ansatz 1 - 6.

orbitals

$$\psi_{coh} = e^{-\alpha_1(r_{1A}+r_{1B}+r_{1C}+r_{2A}+r_{2B}+r_{2C})+\gamma r_{12}}, \quad (7)$$

(Ansatz 1) which is a generalization of the Heitler-London function for the case of the  $H_2^+$  molecular ion or the  $H_2$  molecule; it contains two variational parameters  $\alpha_1, \gamma$  both of them having a meaning of charge (anti)screening. Variational energy as well as the corresponding values of the parameters are presented in Table I. It is already a striking fact that even at  $R_{eq} = 1.65$  a.u. which is essentially larger than the Bohr radius the function (7) leads to a binding of the  $(3p2e)$  system with sufficiently large ionization energy  $\sim 0.12$  a.u. ( $H_3^+ \rightarrow H_2 + p$ )<sup>4</sup>.

## 2. Incoherent interaction

Another natural mechanism of interaction is when each electron "sees" a single charge center, thus, realizing an incoherent interaction. In fact, it corresponds to the interaction of two hydrogen atoms and proton,  $H + H + p$ . Such a mechanism has to be dominant at large internuclear distances in comparison to a characteristic length of the electron-proton interaction of the order of 1 a.u. = 1 Bohr radius. A simplest realization of this mechanism is given by

$$\psi_{incoh} = (1 + P_{12}) \sum_{\text{perm}\{A,B,C\}} e^{-\alpha_1(r_{1A}+r_{2B})+\gamma r_{12}}, \quad (8)$$

<sup>4</sup> In order to calculate the ionization energy we use the  $H_2$  total energy -1.1745 a.u. (rounded) found in [23]

(Ansatz 2) which is a generalization of the Hund-Mulliken function for  $H_2^+$  ion or  $H_2$  molecule, it contains two variational parameters  $\alpha_1, \gamma$  having a meaning of charge (anti)screening. Variational energy as well as the corresponding values of the non-linear parameters  $\alpha_1, \gamma$  are presented in Table I. At  $R_{eq} = 1.65$  a.u. which is essentially larger than the Bohr radius, the function (8) leads to a binding of the  $(3p2e)$  system with sufficiently large ionization energy  $\sim 0.12$  a.u. <sup>4</sup>. The parameter  $\gamma$  takes a negative value indicating the effective attraction of the electrons in this mechanism.

### 3. (almost)Incoherent interaction

This mechanism of interaction appears when two electrons "see" the same charge center interacting coherently, then, the interaction with two other charged centers appears as a result of the exchange interaction. In fact, it corresponds to the interaction of negative hydrogen ion with two protons,  $H^- + 2p$ . Such a mechanism has to be important at large internuclear distances comparing to a characteristic length of the electron-proton interaction of the order of 1 a.u. = 1 Bohr radius. It has to be suppressed due to a small probability of the coherent interaction of two electrons with same proton. A simplest realization of this mechanism is given by

$$\psi_{(a)incoh} = (1 + P_{12}) \sum_{\text{perm}\{A,B,C\}} e^{-\alpha_1(r_{1A}+r_{2A})+\gamma r_{12}}, \quad (9)$$

(we call it the Ansatz 3). Perhaps, it is not surprising that such a trial function does not lead to a binding (see Table I).

### 4. $H_2$ -molecule + proton interaction

In this case both electrons "see" two protons forming  $H_2$  molecule which interacts with proton. Though the interproton distance  $R_{eq} = 1.65$  a.u. for  $H_3^+$  is larger than the equilibrium distance for the  $H_2$  molecule, which is equal to  $\sim 1.4$  a.u., it can be described by the Heitler-London function for the  $H_2$  molecule. Eventually, as a realization of this mechanism we choose

$$\psi_{H_2} = (1 + P_{12}) \sum_{\text{perm}\{A,B,C\}} e^{-\alpha_1(r_{1A}+r_{1B}+r_{2A}+r_{2B})+\gamma r_{12}}, \quad (10)$$

(Ansatz 4) which contains two variational parameters  $\alpha_1, \gamma$  having a meaning of charge (anti)screening. Variational energy as well as the corresponding values of the non-linear parameters  $\alpha_1, \gamma$  are presented in Table I. The function (10) leads to a binding with sufficiently large ionization energy  $\sim 0.15$  a.u. It is worth noting that an attempt to improve a description of the  $H_2$  molecule by replacing the Heitler-London function by the Guillemin-Zener one

$$e^{-\alpha_1(r_{1A}+r_{1B}+r_{2A}+r_{2B})} \rightarrow e^{-\alpha_{1,1}(r_{1A}+r_{1B})-\alpha_{1,2}(r_{2A}+r_{2B})}$$

leads to unessential improvement in ionization energy  $\sim 0.16$  a.u. <sup>4</sup>.

### 5. $H_2^+$ -ion + H-atom interaction

In this case one electron "sees" two protons forming  $H_2^+$  ion and the second electron "sees" the third proton forming H-atom. The interproton distance  $R_{eq} = 1.65$  a.u. for  $H_3^+$  is smaller than the equilibrium distance for the  $H_2^+$  ion, which is equal to  $\sim 2$  a.u.,  $H_2^+$  contribution can be described by the Heitler-London function for the  $H_2^+$  ion. Eventually, as a realization of this mechanism we choose

$$\psi_{H_2^+H} = (1 + P_{12}) \sum_{\text{perm}\{A,B,C\}} e^{-\alpha_1(r_{1A}+r_{1B})-\alpha_6 r_{2C}+\gamma r_{12}}, \quad (11)$$

(Ansatz 5) which contains three variational parameters  $\alpha_1, \alpha_6, \gamma$  having a meaning of charge (anti)screening. This function can be considered as a generalization of the celebrated Guillemin-Zener function written for the  $H_2^+$ -ion and the  $H_2$ -molecule. Variational energy as well as the corresponding values of the parameters are presented in Table I. The function (11) leads to a binding with sufficiently large ionization energy  $\sim 0.14$  a.u. <sup>4</sup> which is nevertheless smaller than one for the Ansatz 4. The parameter  $\gamma$  is close to zero indicating effectively the small repulsion of the electrons.

### 6. Generic interaction

Naturally, a general mechanism of interaction is related to interaction of an electron with a proton (or another electron) with its particular (anti)screening due to the presence of other charges. A simplest realization of this mechanism is given by the function (6) (see above). The variational parameters consist of non-linear parameters  $\alpha_{1-6}$  and  $\gamma$  which characterize

the (anti)screening of the Coulomb charges. Appropriate degeneration of these parameters allow us to reproduce different mechanisms of interaction 1.-5. Variational energy as well as the corresponding values of the parameters are presented in Table I. The function (6) leads to a binding with quite high ionization energy  $\sim 0.17$  a.u.<sup>4</sup>.

## B. Mixed mechanisms

In previous subsection we identified possible single mechanisms of interactions which occur in the system of three static protons and two electrons, (3p2e). Based on the values of ionization (binding) energies these mechanisms can be classified coming from the highest ionization energy at *Generic interaction* mechanism (Ansatz 6.) followed by the mechanism  $H_2^+$ -ion + *H-atom interaction* (Ansatz 5.) and then *H<sub>2</sub>-molecule + proton interaction* (Ansatz 4.) . The goal of this subsection is to consider different superpositions of single mechanisms. The mechanism *(almost)Incoherent interaction* ( $H^- + 2p$ , Ansatz 3.) is excluded as one giving no binding to the (3p2e) system. In all mixed mechanisms the *Generic interaction* mechanism will be always present as one giving the highest ionization energy among single mechanisms.

### 1. *Generic interaction plus coherent interaction*

Let us consider a superposition of the *Generic interaction* (Ansatz 6.) and *Coherent interaction* (Ansatz 1.) (see [11])

$$\psi_{61} = \psi_G + A_{coh}\psi_{coh} . \quad (12)$$

Formally, the trial function  $\psi_{61}$  depends on ten parameters (one linear and 9 non-linear). The results are presented in Table II. It is interesting to note that the non-linear parameters are almost unchanged in comparison to the parameters of the individual Ansätze 1. and 6. with a single exception of the parameter  $\tilde{\gamma}$ . If it is compared with the Ansatz 6. this Ansatz increases the ionization energy to  $\sim 0.001$  a.u.

	$E$ (Ry)	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$	$\alpha_5$	$\alpha_6$	$\gamma$	$A$	$\tilde{\alpha}$	$\tilde{\gamma}$
Generic Ansatz (6)	-2.680 7	-0.00353	0.18548	1.4245	1.0471	0.15082	0.58912	0.21632	-	-	-
(6) $\oplus$ (7)	-2.683 2	-0.00294	0.21022	1.3849	1.0199	0.17103	0.59084	0.26044	-0.51154	0.59589	0.86229
(6) $\oplus$ (8)	-2.683 5	-0.02840	0.19525	1.4780	1.06860	0.12045	0.52108	0.24008	-0.03987	1.71230	0.69991
(6) $\oplus$ (11) ( $\text{H}_2^+ + \text{H}$ )	-2.685 4	-0.05699	0.22600	1.40290	1.04611	0.17386	0.55836	0.14867	-1.52370	1.50704	-1.21701
										1.10855	
(6) $\oplus$ (10) ( $\text{H}_2$ )	-2.686 4	0.00515	0.19795	1.4043	1.03200	0.13466	0.59350	0.13686	-2.34310	0.99547	-0.46046
(6) $\oplus$ (10) ( $\text{H}_2$ ) $\oplus$ (11) ( $\text{H}_2^+ + \text{H}$ )	-2.686 852	0.00040	0.23034	1.42450	1.00418	0.12283	0.56933	0.13409	-2.34400	0.94900	-0.55946
									0.16243	1.72960	-0.87202
										0.066457	
Best value [13] (rounded)	-2.687 671										

TABLE II: The ground state energy of  $\text{H}_3^+$  at  $R_{eq} = 1.65$  a.u. and the non-linear variational parameters in  $[a.u.]^{-1}$  corresponding to the trial function (6) and different degenerations of it. For the case (6) +  $\text{H}_2^+ + \text{H}$ , the  $\alpha$  parameter in the second row corresponds to the effective charge for the H-atom part.

## 2. *Generic interaction plus incoherent interaction*

Let us consider a superposition of the *Generic interaction* (Ansatz 6.) and *Incoherent interaction* (Ansatz 2.)

$$\psi_{62} = \psi_G + A_{incoh}\psi_{incoh} . \quad (13)$$

Formally, the trial function  $\psi_{62}$  depends on ten parameters (one linear and 9 non-linear). The results are presented in Table II. It is interesting to note that the non-linear parameters of the Ansatz 6. in (13) are almost unchanged in comparison to the parameters of the individual Ansatz 6. with a single exception of the parameter  $\alpha_1$  while the parameters of the Ansatz 2. are changed significantly. If it is compared with the Ansatz 6. this Ansatz increases the ionization energy to  $\sim 0.002$  a.u.

## 3. *Generic interaction plus $H_2$ -molecule + proton interaction*

Let us consider a superposition of the *Generic interaction* (Ansatz 6.) and  *$H_2$ -molecule + proton interaction* (Ansatz 4.)

$$\psi_{64} = \psi_G + A_{H_2}\psi_{H_2} . \quad (14)$$

Formally, the trial function  $\psi_{64}$  depends on ten parameters (one linear and 9 non-linear). The results are presented in Table II. It is interesting to note that the non-linear parameters of the Ansatz 6. in (14) are almost unchanged in comparison to the parameters of the individual Ansatz 6. with a single exception of the parameter  $\gamma$  while the parameters of the Ansatz 3. are changed insignificantly. If it is compared with the Ansatz 6. this Ansatz increases the ionization energy to  $\sim 0.003$  a.u. In comparison with the most accurate total energy this Ansatz reproduces 3 figures.

## 4. *Generic interaction plus $H_2^+$ -ion + H-atom interaction*

Let us consider a superposition of the *Generic interaction* (Ansatz 6.) and  *$H_2^+$ -ion + H-atom interaction* (Ansatz 5.)

$$\psi_{65} = \psi_G + A_{H_2^++H}\psi_{H_2^++H} . \quad (15)$$

Formally, the trial function  $\psi_{65}$  depends on eleven parameters (one linear and 10 non-linear). The results are presented in Table II. It is interesting to note that the non-linear parameters of the Ansatz 6. in (15) are almost unchanged in comparison to the parameters of the individual Ansatz 6. with a single exception of the parameter  $\gamma$  while the parameters of the Ansatz 4. are changed significantly, especially the parameter  $\gamma$ . If it is compared with the Ansatz 6. this Ansatz increases the ionization energy to  $\sim 0.002$  a.u. In comparison with the most accurate total energy this Ansatz reproduces 3 figures.

#### 5. *Generic interaction plus $H_2$ -molecule + proton interaction plus $H_2^+$ -ion + H-atom interaction*

Following the analysis of the variational total energies found in single mechanisms of binding of the  $H_3^+$ -ion we arrive at the hierarchy: *Generic interaction* (Ansatz 6.) goes first, then  *$H_2^+$ -ion + H-atom interaction* (Ansatz 5.) is the second and  *$H_2$ -molecule + proton interaction* (Ansatz 4.) as the third. In turn, the analysis of the variational total energies found in mixed mechanisms of binding involving two mechanisms we arrive again at a conclusion that above-mentioned three mechanisms of binding play a dominant role. Thus, a natural move is to consider a superposition of these three mechanisms of binding: the *Generic interaction* (Ansatz 6.),  *$H_2^+$ -ion + H-atom interaction* (Ansatz 5.) and  *$H_2$ -molecule + proton interaction* (Ansatz 4.),

$$\psi_{645} = \psi_G + A_{H_2} \psi_{H_2} + A_{H_2^++H} \psi_{H_2^++H} . \quad (16)$$

The trial function  $\psi_{645}$  depends on fourteen parameters (two linear and 12 non-linear). The results are presented in Table II. It is interesting to note that remarkably the non-linear parameters of the Ansatz 6. in (16) are almost unchanged in comparison to the parameters of the individual Ansatz 6. itself as well as in Ansatz (15) and Ansatz (14) with a single exception of the parameter  $\gamma$  which nevertheless remains almost unchanged for Ansatz (15), Ansatz (14) and Ansatz (16). The non-linear parameters of the Ansatz 5. are slightly changed in the Ansatz (15) and Ansatz (16). We consider this as an indication that the *Generic interaction* is described adequately by the Ansatz 6. (6) as well as the  *$H_2$ -molecule + proton interaction* is described adequately by the Ansatz 4. (10). The non-linear parameters of the Ansatz 5. are changed significantly, especially the parameter  $\gamma$ , comparing to ones in

the Ansatz (14) and Ansatz (16). Also the non-linear parameters of the Ansatz 4. in the Ansatz (14) and Ansatz (16) are very much different. We consider this as an indication that the mechanism of the  $H_2^+$ -ion +  $H$  interaction is described inadequately by the Ansatz 4. (11). Perhaps, for  $H_2^+$ -ion part the Heitler-London function for  $H_2^+$  should be replaced by more adequate Guillemin-Zener function

$$e^{-\alpha_{4,1}(r_{1A}+r_{1B})} \rightarrow e^{-\alpha_{4,1}^{(1)}r_{1A}-\alpha_{4,1}^{(2)}r_{1B}}$$

(see (11)). It will be done elsewhere.

If the Ansatz (16) is compared with the Ansatz 6. this Ansatz leads to increase in the ionization energy to  $\sim 0.003$  a.u. Making a comparison of the obtained variational total energy with the most accurate total energy it appears that this Ansatz provides a deviation from the best known energy which is equal to  $\sim 0.0004$  a.u. (see Table III).

## V. RESULTS

In Table III we present the results for the ground state energy at interproton equilibrium distance of the  $H_3^+$  molecular ion obtained previously using different methods. It can be seen that the Born-Oppenheimer ground state energy obtained using the trial function (16) is the most accurate (the lowest) energy obtained with a few parametric functions. In particular, the trial function (16) gives a lower energy than the energies obtained with the explicitly correlated functions based on both Gaussians in  $r_{12}$  [24] and linear in  $r_{12}$  [25], when a relatively small number of terms with non-linear parameters is involved. The trial function (16) is more accurate than all(!) traditional CI calculations which were performed before 1990 (see [26]) even including the one with the largest set of 100 configurations [27, 28]<sup>5</sup> and as well as [32], however, being worse than the largest CI calculation ever performed [33] (700 configurations). In those CI calculations no explicit correlation was included. The trial function (16) is more accurate than some CI calculations with explicitly involved  $r_{12}$  dependence [34] (36 configurations) and [35] (192 configurations) but gets worse when (much) larger number of configurations is included [36-37]. In general, the 14-parametric trial function (16) gives the eighth best result among known in literature so far (see Table III)

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<sup>5</sup> for a list of 42 calculations of the ground state energy of  $H_3^+$  in the period 1938-1992 see Ref.[26], for a list of selected *ab-initio* calculations till 1995, see [5]



being incomparably simpler with respect to all known trial functions. It is worth noting that the 7-parametric trial function (6) [11] gives the thirteenth best result among known in literature (see Table III).

The list of major expectation values obtained using different trial functions (6), (12) - (16) and its comparison with results of other calculations is given in Table IV. A reasonable agreement for the expectation values is observed. In particular, for the expectation values  $\langle 1/r_{1A} \rangle$ ,  $\langle x^2 \rangle$ ,  $\langle z^2 \rangle$  and  $\langle r^2 \rangle$  agreement within  $\sim 1\%$  with ours and all other calculations is observed, including ones obtained in the large CISD-R12 calculations [25]. Also, for the expectation value of  $\langle 1/r_{12} \rangle$  we have an agreement in the first significant digit with other calculations, and we are also in close agreement to the value obtained with the correlated Gaussian (unrestricted) wavefunction with 15 terms [24]. For the expectation values  $\langle 1/r_{1A} \rangle$  and  $\langle z^2 \rangle$  we observe agreement with other calculations in 3 and 2 significant digits, respectively. These facts seem to indicate that the presented expectation values are very accurate, corroborating the quality of the trial functions (6), (12)-(16) which gives 2-3 s.d. correctly. It is worth noting that since there are no criteria about accuracy of the obtained expectation values, we can only comment about the agreement within our results based on different trial functions and those obtained by other approaches. Since the exact phase of the ground state eigenfunction is uniformly approximated by the phases the trial functions (6), (12) - (16) we guess that the relative accuracy reached in variational energy has to be similar to the relative accuracy in an expectation value. It implies that the expectation value based on (6), (12) - (15) should provide two significant digits correctly, while (16) should give three significant digits (see Table IV). Following this assumption we can state that  $\langle r_{12} \rangle = 1.9(9)$  a.u.,  $\langle 1/r_{12} \rangle = 0.62(6)$  (a.u.)<sup>-1</sup> (hence, in Ref.[27] a single figure was found correctly),  $\langle 1/r_{1A} \rangle = 0.85(5)$  (a.u.)<sup>-1</sup> (it agrees in 2 figures with all previous calculations, see Table IV),  $\langle x_1^2 \rangle = 0.76(1)$  (a.u.)<sup>2</sup> (it agrees in 2 figures with all previous calculations, see Table IV),  $\langle z_1^2 \rangle = 0.54(2)$  (a.u.)<sup>2</sup> (it agrees in 2 figures with all previous calculations except (12) and (14), see Table IV),  $\langle r_1^2 \rangle = 2.0(6)$  (a.u.)<sup>2</sup> (it agrees in 2 figures with all previous calculations, see Table IV)

$E$ (a.u.)	$R$ (a.u.)	method	reference
-1.339 7	1.66	CI-GTO, > 120 configs	[29] (1970)
-1.306 29	1.65	GG, 3 terms, 5 non-linear params	[24] (1973)
-1.327 25	1.65	GG, 6 terms, 7 non-linear params	
-1.331 47	1.65	GG, 10 terms, 9 non-linear params	
-1.332 29	1.65	GG, 15 terms, 11 non-linear params	
-1.334 382	1.65	R12, 10s basis set	[25] (1993)
-1.334 632	1.65	R12, 30s basis set	
-1.340 34	1.65	7-Parametric Trial Function (6)	[11] (2011)
-1.340 5	1.6405	CI -GTO, 48 configs	[27] (1971)
-1.340 5	1.65	CI -STO, 100 configs	[28] (1971)
-1.342 72	1.65041	CI-GTO, 108 terms	[31] (1985)
-1.342 784	1.6504	CI-GTO, $8s3p1d/[6s3p1d]$ basis set	[32] (1978)
-1.343 40	1.6504	CI-GTO, $10s4p2d$ basis set	[33] (1990)
-1.343 822	1.65	CI-GTO, 700 terms	[34] (1990)
-1.342 03	1.6504	CI with r12, 36 configs	[35] (1982)
-1.343 422	1.6504	CI with r12, 192 configs	[36] (1984)
-1.343 426	1.65	14-parametric Trial function (16)	present
-1.343 500	1.6504	CI with r12, $13s3p/[10s2p]$ basis set	[37] (1988)
-1.343 828	1.65	CI with r12, $13s5p3d$ basis set.	[38] (1990)
-1.343 835	1.65	R12, $30s20p12d9f$ basis set	[25] (1993)
-1.343 35	1.65	GG, 15 terms, 135 non-linear params	[24] (1973)
-1.343 835 624	1.65	GG, 600 terms	[14] (1995)
-1.343 835 625 02	1.65	ECSG, 1000 terms	[13] (2009)

TABLE III: A selection of the calculations for the Born-Oppenheimer ground state energy at equilibrium distance of  $\text{H}_3^+$ . Record calculations of Ref. [13] (2009) and Ref.[14] (1995). CI denotes Configuration Interaction, STO - Slater Type Orbitals, GTO - Gaussian Type Orbitals, GG - correlated Gaussians (Gaussian Geminals), R12 - the CI calculation augmented by terms linear in  $r_{12}$ , ECSG - Explicitly Correlated Spherical Gaussian functions. Our present results: Trial Function (16) with fourteen parameters optimized.

Expectation Value	Trial Function	Others
$\langle r_{12} \rangle$	2.0032 (6)	
	1.9931 (12)	
	1.9927 (13)	
	1.9831 (15)	
	1.9868 (14)	
	1.9864 (16)	
$\langle 1/r_{12} \rangle$	0.6315 (6)	0.59415 <sup>a</sup>
	0.6302 (12)	0.62636 <sup>c</sup>
	0.6293 (13)	
	0.6273 (15)	
	0.6280 (14)	
	0.6261 (16)	
$\langle 1/r_{1A} \rangle$	0.8548 (6)	0.85519 <sup>c</sup>
	0.8549 (12)	0.8553 <sup>e</sup>
	0.8553 (13)	
	0.8555 (15)	
	0.8556 (14)	
	0.8553 (16)	

TABLE IV: Expectation values (in a.u.) for the  $H_3^+$  ion in its ground state obtained with the trial functions (6) and (12-16) . Corresponding results obtained with other methods are displayed for comparison. The coordinates  $x, y, z$  and  $r$  are measured from the center of the equilateral triangle formed by protons. <sup>a</sup> Ref.[27] CI-43; <sup>b</sup> CI wavefunction (I) in Ref.[28]; <sup>c</sup> Correlated Gaussian (unrestricted) wavefunction with 15 terms in Ref.[24]; <sup>d</sup> CI wavefunction in Ref.[30]; <sup>e</sup> CISD-R12 wavefunction with the  $10s8p6d4f$  basis set in Ref.[25].

## VI. CONCLUSION

We identified five mechanisms of interaction leading to a binding in the Coulomb problem of two electrons in the field of three fixed charged centers ( $2e3p$ ) in equilibrium geometry - the charged centers form the equilateral triangle with side 1.65 a.u. Among these five

Expectation Value	Trial Function		Others
$\langle x^2 \rangle = \langle y^2 \rangle$	0.7711	(6)	0.75818 <sup>a</sup>
	0.7666	(12)	0.7595 <sup>b</sup>
	0.7610	(13)	0.75913 <sup>c</sup>
	0.7588	(15)	0.75968 <sup>d</sup>
	0.7609	(14)	0.7605 <sup>e</sup>
	0.7613	(16)	
$\langle z^2 \rangle$	0.5399	(6)	0.54802 <sup>a</sup>
	0.5337	(12)	0.5451 <sup>b</sup>
	0.5420	(13)	0.54085 <sup>c</sup>
	0.5375	(15)	0.54179 <sup>d</sup>
	0.5348	(14)	0.5396 <sup>e</sup>
	0.5420	(16)	
$\langle r^2 \rangle$	2.0822	(6)	2.06442 <sup>a</sup>
	2.0669	(12)	2.0640 <sup>b</sup>
	2.0640	(13)	2.05911 <sup>c</sup>
	2.0550	(15)	2.06114 <sup>d</sup>
	2.0565	(14)	
	2.0646	(16)	

TABLE IV: *Continued.* Expectation values (in a.u.) for the  $H_3^+$  ion in its ground state obtained with the trial functions (6) and (12-16) . Corresponding results obtained with other methods are displayed for comparison. The coordinates  $x, y, z$  and  $r$  are measured from the center of the equilateral triangle formed by protons. <sup>a</sup> Ref.[27] CI-43; <sup>b</sup> CI wavefunction (I) in Ref.[28]; <sup>c</sup> Correlated Gaussian (unrestricted) wavefunction with 15 terms in Ref.[24]; <sup>d</sup> CI wavefunction in Ref.[30]; <sup>e</sup> CISD-R12 wavefunction with the  $10s8p6d4f$  basis set in Ref.[25].

mechanisms three lead to a strongest binding:  $H_2$ -molecule plus proton,  $H_2^+$  ion plus  $H$ -atom and generic. Each mechanism of interaction is easily modeled by a certain two-three-seven-parametric wavefunction, respectively, which is taken as a variational trial function. Corresponding variational energies are certainly the lowest ones among two-three and seven parametric trial functions, respectively (see Table III).

In particular, a simple and compact 7-parametric variational trial function (6) (generic mechanism) already provides surprisingly accurate Born-Oppenheimer energy for the ground state of such a complicated molecular system as  $\text{H}_3^+$ . The minimum energy is found to be  $E = -1.34034$  a.u. at an equilibrium interproton distance  $R = 1.65$  a.u. This result for the energy is the most accurate among the values obtained with several parametric trial functions of GG type [24] (Gaussian in  $r_{12}$ ), when a relatively small number of terms and non-linear parameters are involved, see Table III. In particular, it is more accurate than the energies obtained with the explicitly correlated approaches of Ref.[25].

It seems natural to advance by considering a superposition of three dominant mechanisms of binding like it was done in [7] for  $\text{H}_2$ -molecule,

$$\Psi = \psi_G + A_{H_2}\psi_{H_2} + A_{H_2^++H}\psi_{H_2^++H} ,$$

as well as a superposition of two dominant mechanisms of binding. It immediately gives an essential improvement in the energy (see Table II). In particular, the function (16) (a superposition of three dominant mechanisms), which contains fourteen variational parameters, allows us to get a more accurate result for the energy than one obtained by Preiskorn-Woznicki [36] in CI with  $r_{12}$  included using 192 configurations. Our result is slightly worse than one by [37] in CI with  $r_{12}$  included, using  $13s3p/[10s2p]$  basis set.

The obtained energy (16) is among eight the most accurate variational results ever calculated so far but using incomparably much more simple trial function. The major expectation values in Table IV are gradually changed with the moves from one Ansatz to another seemingly demonstrating a convergence. It is clearly seen that in any expectation value (as well as in BO energy) two significant digits remain stable, they do not depend on the Ansatz considered. Thus, it can be stated that two significant digits in any expectation value are calculated reliably. Without doubt, the trial function (6) can be used to study potential energy surface. It seems that two significant digits are guaranteed. As an illustration on Fig. 2 the potential curve  $E$  vs  $R$  is presented. It is based on a linear superposition of Ansatz (6) and (7).

It is worth emphasizing that the main virtue of functions (6), (16) is their compactness. A similar analysis of binding can be carried out for low-lying states and corresponding wavefunctions written. In particular, the function (6) can be easily modified for a study of spin-triplet states, as well as the low-lying states with non-vanishing magnetic quantum

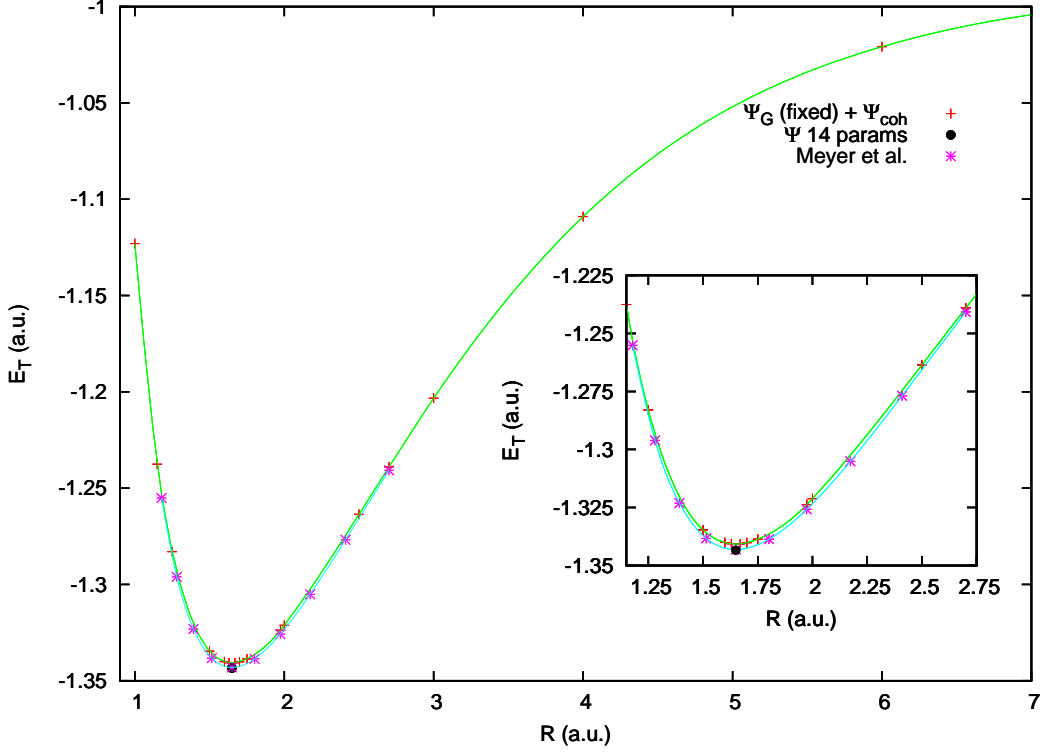


FIG. 2: Potential Energy Curve for the  $\text{H}_3^+$  ion in triangular equilateral configuration as a function of the triangle size  $R$  obtained with the 7+3 parameter Ansatz (12) (see [11]). Results by Meyer *et al.* obtained using CI  $10s, 4p, 2d$  GTO basis [33] are shown for comparison. The energy of (16) at equilibrium is marked by bullet

number. A generalization to more-than-two electron molecular systems seems also straightforward.

In order to conclude we must mention that a domain of applicability of BO approximation of the zero order (infinitely massive particles of positive charge are assumed) is limited. This question can be thorough studied on the example of two-center problem exploring the  $\text{H}_2^+$ ,  $\text{D}_2^+$ ,  $\text{T}_2^+$  ions. We used the ground state energies and the expectation values for the internuclear distance obtained in the Lagrange-mesh method for two-center problem  $E_{BO}, R_{eq}$  and the  $\text{H}_2^+$ ,  $\text{D}_2^+$ ,  $\text{T}_2^+$  ions [39] with relative accuracy  $\sim 10^{-12}$  (for energies) and  $\sim 10^{-7}$  (for the internuclear distances) found the fits

$$E(M, m_e) - E_{BO} = 0.468436 \sqrt{\frac{m_e}{M}} \quad , \quad \langle R_{NN}(M, m_e) \rangle - R_{eq} = 2.84964 \sqrt{\frac{m_e}{M}} \quad ,$$

where  $m_e$  is the electron mass and  $M$  is the mass of a heavy particle. Hence, the finite-mass corrections begin to contribute to the 2-3rd significant digit. One way to include the finite-

mass corrections is to introduce the zero energy state corresponding to the lowest energy state of nuclear motion. In this case the zero energy is equal to the BO ground state energy of the zero order (a minimum at the potential curve) plus the first vibrational energy. One of the ways to find the first vibrational state is to consider a harmonic approximation of the bottom of the potential curve. One can see that the zero energy coincides to the non-BO energy up to four-five significant digits. In order to get further improvement it is necessary to go beyond harmonic approximation, also taking into account non-adiabatic corrections and write more accurate BO trial functions. It makes the overall analysis complicated. We think it is more relevant to consider an alternative way treating the problem solving the exact 3-body Schrödinger equation without any type of BO approximation similar to what was done for example in [41]. In particular, it would allow to study the essential effects which do not exist in BO approximations like the electric quadrupole transitions.

Similar consideration can be performed for three-center problem finding  $E_{BO}, R_{eq}$  and for the  $H_3^+, D_3^+, T_3^+$  ions. From non-BO calculations made in [40] it can be seen that finite-mass corrections are essentially larger than for ones for two-center case. They contribute to the 2-3rd significant digits to the ground state energies of  $H_3^+, D_3^+, T_3^+$  and the expectation value for internuclear distance,

$$E(M, m_e) - E_{BO} = 1.27232 \sqrt{\frac{m_e}{M}} \quad , \quad \langle R_{NN}(M, m_e) \rangle - R_{eq} = 4.21669 \sqrt{\frac{m_e}{M}} \quad ,$$

where  $m_e$  is the electron mass and  $M$  is the mass of a heavy particle. Taking into account the lowest vibrational energy found in [5] the agreement between zero energy and non-BO ground state energy [40] is improved up to 4th significant digit only. We would consider it as indication that the exact, 5-body Schroedinger equation has to be treated when going beyond the fifth significant digit in energy. The consideration presented in [40] shows that is feasible. It seems evident that the dominant mechanisms of interaction leading to binding found in BO approximation will remain dominant beyond of it in non-BO consideration. We think that namely in such an approach the radiative transitions in the  $H_3^+$  ion have to be studied.

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